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Transient Absorption Spectra and Lifetimes of Benzophenone Ketyl Radicals in the Excited State

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The absorption spectrum of benzophenone ketyl radicals in the D_1 excited state (BPH•(D_1)), generated by hydrogen abstraction of triplet benzophenone from cyclohexane as a solvent and the sequential excitation of the benzophenone ketyl radical in the ground state (BPH•(D_0)), was directly observed using nanosecond−picosecond two-color two-laser flash photolysis. The whole spectral shape of BPH•(D_1) with peaks at 350 and 480 nm was detected for the first time. The absorption spectra and lifetimes were obtained for a series of ketyl radicals (BPDH•) in the D_1 excited state (BPDH•(D_1)) of benzophenone derivatives (BPDs) such as 4-methyl-, 4,4′-dimethyl-, 4-methoxy-, 4,4′-dimethoxy-, 4-trifluoromethyl-, 4-fluoro-, 4,4′-difluoro-, 4-chloro-, and 4-bromobenzophenones. The absorption spectra of BPDH•(D_1) were found to be significantly affected by the number and electronic character of the substituents on the phenyl ring. BPDH• which has a large conformational change between the ground and emitting states showed a shorter D_1-state lifetime. The decay processes of the D_1 state including the radiative and nonradiative relaxation processes and the chemical reaction are discussed quantitatively.

Introduction

Recent progress with a short-pulse laser has revealed various dynamic processes of short-lived excited states of various molecules.[1] The excited state of radicals is an attractive subject from both photochemical and photophysical aspects. Many studies of the benzophenone ketyl radical (BPH•) have been carried out with absorption and emission spectroscopies to elucidate electronic structures and chemical properties in the condensed phase.[2−13]

The fluorescence of excited radicals due to the $D_1 \rightarrow D_0$ transition is detectable in the condensed phase at room temperature. Fluorescence spectra have been reported for excited radicals such as diphenylmethyl,[14] naphthylmethyl,[15] anthrylmethyl,[16] diphenylketyl,[4−13] and acetophenone ketyl[17] radicals. On the other hand, limited numbers of absorption spectra have been observed for the excited radicals.[9,14,17] To the best of our knowledge, there is only one report on the absorption spectrum of BPH• in the D_1 excited state (BPH•(D_1)). Nagarajan and Fessenden reported the $D_n \leftarrow D_1$ absorption spectra of benzophenone and 4,4′-dichlorobenzophenone ketyl radicals with a peak around 350 and 370 nm, respectively, in cyclohexane using nanosecond laser photolysis at room temperature.[9] However, those absorption spectra were limited to a rather narrow wavelength region (340−420 nm) because of the scattering of the laser pulse. Additionally, it is difficult to detect the absorption of BPH•(D_1) using nanosecond lasers because the lifetime of the $D_1 \rightarrow D_0$ fluorescence is found to be only 2.0 ns.[9]

In the present work, we applied nanosecond−picosecond two-color two-laser flash photolysis to detect the reliable absorption spectrum of BPH•(D_1) in the UV−visible region. The whole spectral shape of BPH•(D_1) with peaks at 350 and 480 nm was detected for the first time. Absorption spectra were also obtained for a series of benzophenone derivative (BPD) ketyl radicals (BPDH•) in the D_1 excited state (BPDH•(D_1)). The absorption spectra of BPDH•(D_1) were revealed to be significantly affected by the number and electronic character of the substituents on the phenyl ring. The effect of the substituent on the lifetime of BPDH•(D_1) (τ) was also confirmed. The decay processes of BPDH•(D_1) such as the radiative and nonradiative relaxation processes and the chemical reaction are discussed quantitatively. It was confirmed that the BPDH• with a large conformational change between the D_0 and D_1 states has a shorter lifetime. The distorted conformation in the D_1 state enhances the decay process from the D_1 state.

Experimental Section

The two-color two-laser flash photolysis experiment was carried out using the fourth harmonic oscillation (266 nm) of a nanosecond Nd^{3+}:YAG laser (Quantel, Brilliant; 5-ns full width at half-maximum (fwhm)) as the first laser and the second harmonic oscillation (532 nm) of a picosecond Nd^{3+}:YAG laser (Continuum, RGA69-10; 30-ps fwhm, 10 Hz) as the second laser. The delay time of the two laser flashes was adjusted to 1 μs by four-channel digital delay/pulse generators (Stanford Research Systems, model DG 535). The breakdown of Xe gas generated by the fundamental pulse of the picosecond Nd^{3+}:YAG laser was used as a probe light. Transient absorption spectra and kinetic traces were measured using a streak camera (Hamamatsu Photonics C7700) equipped with a charge-coupled device (CCD) camera (Hamamatsu Photonics C4742-98) and were stored on a personal computer (PC). To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were employed. The samples were allowed to be flowed into a

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TABLE 1: Stokes Shifts for BPDH• (ν_{SS}), Lifetimes of Transient Absorption (τ) and Fluorescence (τ_f), Rate Constants of the Chemical Reaction (k_C), Rate Constants of the Radiative (k_f) and Nonradiative (k_{IC}) Relaxation Processes, and the Energy Gaps of BPDH• between the D_1 and D_0 States ($\Delta E(D_1 - D_0)$)

ketyl radical	$\nu_{SS}/10^3$ (cm^{-1})	τ (ns)	τ_f (ns)	$k_C/10^8$ (s^{-1})	$k_f + k_{IC}/10^8$ (s^{-1})	$\Delta E(D_1 - D_0)$ (eV)
benzophenone	0.75	2.0 ± 0.1	2.0 ± 0.1	1.7 ± 0.1	3.4 ± 0.1	2.20
4-fluoro-	0.96	1.4	1.3 ± 0.1	*a*	*a*	2.18
4,4′-difluoro-	1.5	0.47	0.47	*a*	*a*	2.12
4-chloro-	0.75	3.3 ± 0.1	3.2 ± 0.1	*a*	*a*	2.16
4,4′-dichloro-	0.72	3.4 ± 0.3	3.4 ± 0.1	1.4 ± 0.1	1.5 ± 0.1	2.11
4-bromo-	0.78	2.1	2.1	2.2 ± 0.1	2.8 ± 0.1	2.16
4,4′-dibromo-	0.69	3.5 ± 0.1	3.6 ± 0.1	1.8 ± 0.1	1.1 ± 0.1	2.10
4-trifluoromethyl-	0.73	4.3 ± 0.3	4.3 ± 0.3	*a*	*a*	2.15
4-methyl-	0.79	1.9 ± 0.1	1.8	*a*	*a*	2.18
4-methoxy-	1.2	0.86 ± 0.04	0.89	*a*	*a*	2.11
4,4′-dimethyl-	0.78	1.7 ± 0.1	1.6	*a*	*a*	2.14
4,4′-dimethoxy-	1.7	0.34 ± 0.02	0.35	*b*	*b*	2.02

[a] Not determined because the recovery of BPDH•(D_0) was not observed due to the overlap of the $D_n \leftarrow D_1$ absorption. [b] The recovery was not observed.

transparent rectangular quartz cell (1.0 × 0.5 × 2.0 cm^3) at room temperature.

For the measurements of both fluorescence spectra and decay profiles, the streak camera was used as the detector.

BPDs were recrystallized two or three times from ethanol before use. Sample solutions were prepared in cyclohexane and deoxygenated with bubbling Ar gas for 30 min before irradiation. All experiments were carried out at room temperature.

Results and Discussion

Generation of Ketyl Radicals. BPDH• was generated by the photoreduction of BPD in cyclohexane. The BPD in the triplet excited state (^{3}BPD) decayed through hydrogen abstraction from cyclohexane to produce BPDH• after the first 266-nm nanosecond laser irradiation (eq 1).[12]

$$\mathrm{BPD} \xrightarrow{h\nu_{266}} {}^3\mathrm{BPD} \xrightarrow{\text{hydrogen abstraction}} \mathrm{BPDH}\bullet \qquad (1)$$

The spectrum of BPH• which has two peaks at 333 and 541 nm agreed with the reported one (Figure 1).[9,12] The substituent intensified the absorption of BPDH• in the near-UV region except for the 4,4′-difluorobenzophenone ketyl radical, of which the band in the near-UV region was broadened. The apparent difference in the absorption spectrum of BPDH• is presumably ascribed to the steric and electronic effects of the substituent group.

Fluorescence Spectra and Lifetime. The generated BPH• was excited at the visible absorption band using the second laser (532 nm, 4 mJ/pulse, 30-ps fwhm) with a delay time of 1 μs after the first laser. Upon excitation, BPH• showed fluorescence with a peak at 564 nm.[17] Similarly, the fluorescence of BPDH• was observed with the second laser irradiation (eq 2).

$$\mathrm{BPDH}\bullet(D_0) \xrightarrow{h\nu_{532}} \mathrm{BPDH}\bullet(D_1) \xrightarrow{h\nu_f} \mathrm{BPDH}\bullet(D_0) \qquad (2)$$

The fluorescence spectra of BPDH• were almost mirror images of the absorption spectra of BPH• (Figure 1). 4,4′-Dimethoxy-, 4,4′-difluoro-, 4-methoxy-, and 4-fluoro-substituted benzophenone ketyl radicals showed larger Stokes shifts than those of the others, suggesting that the structures of these BPDH• species in the D_1 state are largely different from those in the D_0 state.

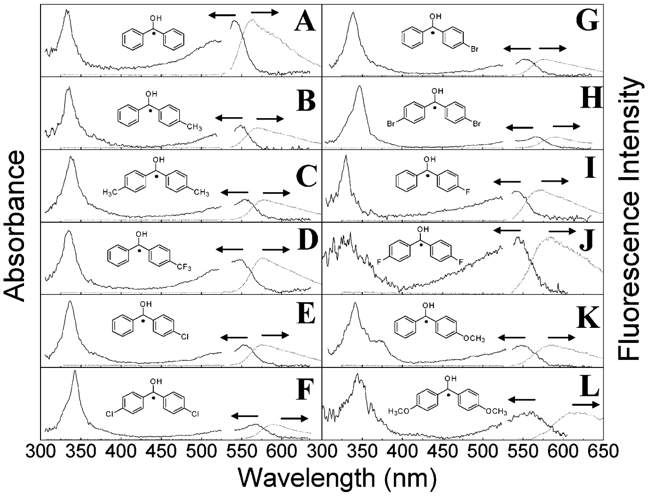


Figure 1. Absorption (solid line) and fluorescence (dotted line) spectra of BPDH•(D_0) in Ar-saturated cyclohexane at room temperature: the absorption spectra were obtained during the 266-nm laser flash photolysis, while the fluorescence spectra were obtained during the 266- and 532-nm two-color two-laser flash photolysis of BPD (A, benzophenone; B, 4-methylbenzophenone; C, 4,4′-dimethylbenzophenone; D, 4-trifluoromethylbenzophenone; E, 4-chlorobenzophenone; F, 4,4′-dichlorobenzophenone; G, 4-bromobenzophenone; H, 4,4′-dibromobenzophenone; I, 4-fluorobenzophenone; J, 4,4′-difluorobenzophenone; K, 4-methoxybenzophenone; and L, 4,4′-dimethoxybenzophenone). The blank around 532 nm in the spectra is due to the residual SHG of the Nd^{3+}:YAG laser.

The energy gaps between the D_1 and D_0 states of BPDH• ($\Delta E(D_1 - D_0)$) were determined from the fluorescence maxima (Table 1). The $\Delta E(D_1 - D_0)$ values are similar for all BPDH• species, except for the 4,4′-dimethoxybenzophenone ketyl radical which has a slightly lower $\Delta E(D_1 - D_0)$ value than the others.

The fluorescence lifetimes (τ_f values) of these ketyl radicals were measured at the peak position of the fluorescence spectra. All fluorescence decay curves fitted well with the single-exponential decay functions (Figure 2A). The measured τ_f value of BPH• is 2.0 ns, which is close to the reported value.[9,12] 4-Chloro-, 4,4′-dichloro-, 4-bromo-, 4,4′-dibromo-, and 4-trifluoromethylbenzophenone derivatives (D_1) showed a larger τ_f value than the others. The fluorescence properties of BPDH•(D_1) such as the lifetime, Stokes shift, and $\Delta E(D_1 - D_0)$ are summarized in Table 1. It is generally admitted that τ_f increases with a decrease in the Stokes shift.[11] This correlation indicates that the conformational change associated with the electronic transition between the D_1 and D_0 states plays an important role in the decay process from BPDH•(D_1) to BPDH•(D_0). It has been reported that the twisting angle of the phenyl ring was responsible for the increase in the decay rate constant.[11]

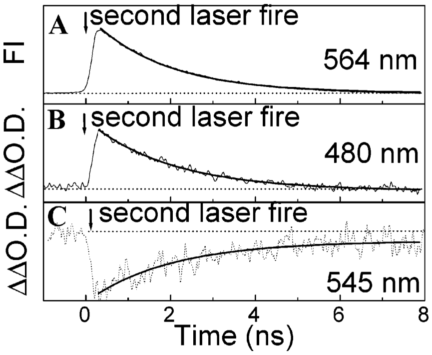


Figure 2. Kinetic traces of fluorescence intensity (FI) at 564 nm (A) and absorption at 545 and 480 nm (B and C, respectively) of BPH•(D$_1$) during the two-color two-laser photolysis.

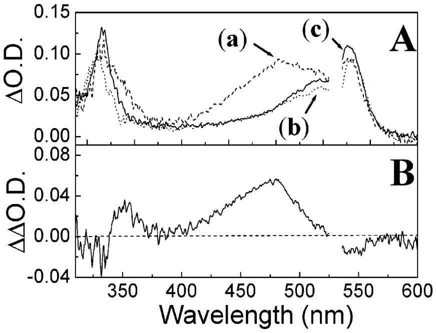


Figure 3. Transient absorption spectra observed at 0.5 (broken line (a)) and 20 (dotted line (b)) ns after the second laser irradiation during the two-color two-laser photolysis (266 and 532 nm) and the spectrum observed during one-laser photolysis (266 nm, solid line (c)) of benzophenone (1.0×10^{-4} M) in Ar-saturated cyclohexane (A). The second laser was irradiated at 1 μs after the first laser pulse. The transient absorption spectrum of BPH•(D$_1$) (B) was given by subtracting spectrum c from spectrum a. The blank around 532 nm in the spectra is due to the residual SHG of the Nd^{3+}:YAG laser.

Therefore, the twisting angle of the phenyl ring seems to be responsible for the increase in the Stokes shift.

Absorption Spectra and Lifetimes of the Ketyl Radical Excited State. Immediately after the second laser irradiation, bleaching of the absorption of BPH• and the growth of new transient absorption peaks at 350 and 480 nm were observed, as shown in Figure 3A. The spectral shape of the new transient species was given by subtracting the spectrum observed before the second laser irradiation from that observed at 0.5 ns after the irradiation (Figure 3B). The τ values of the two absorption peaks at 350 and 480 nm were similar, suggesting that the two absorption bands originated from a single transient species. The τ value estimated from the absorption decay was essentially the same as the τ_f value estimated from the fluorescence decay (Figure 2B). Therefore, these transient absorption bands can be attributed to the $D_n \leftarrow D_1$ transition (Scheme 1). The absorption band of BPH•(D$_1$) in the visible region has never been reported.[9,12,17]

The transient absorption spectrum of BPH•(D$_1$) exhibited two absorption peaks in the near-UV and visible regions (Figure 3B), from which the transition energies from the D$_1$ state to two higher excited doublet states (D$_m$ and D$_n$) were estimated to be 3.4 and 2.5 eV, respectively, and the D$_1$ energy was estimated to be 2.2 eV from the fluorescence maximum. Because the transition energy from the D$_0$ state to the D$_2$ state of BPH• has been reported to be 3.5 eV,[8,9] the energy difference between the D$_1$ and D$_2$ states is 1.3 eV, which is smaller than the $D_n \leftarrow D_1$ transition energies. Therefore, it is suggested that the absorption bands correspond to the $D_m \leftarrow D_1$ and $D_n \leftarrow D_1$ ($m > n > 2$) transitions.

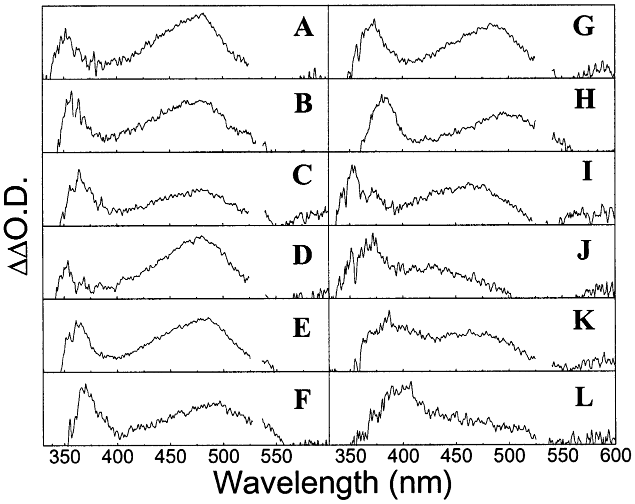
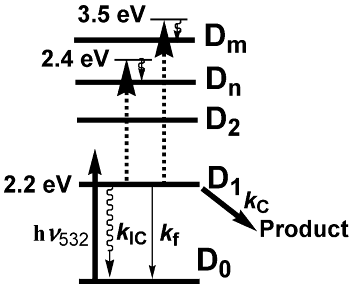


Figure 4. The transient absorption spectra of BPDH•(D$_1$) observed during the two-color two-laser photolysis (266 and 532 nm) of BPD (A, benzophenone; B, 4-methylbenzophenone; C, 4,4′-dimethylbenzophenone; D, 4-trifluoromethylbenzophenone; E, 4-chlorobenzophenone; F, 4,4′-dichlorobenzophenone; G, 4-bromobenzophenone; H, 4,4′-dibromobenzophenone; I, 4-fluorobenzophenone; J, 4,4′-difluorobenzophenone; K, 4-methoxybenzophenone; and L, 4,4′-dimethoxybenzophenone) in Ar-saturated cyclohexane solution. The blank around 532 nm in the spectra is due to the residual SHG of the Nd^{3+}:YAG laser.

SCHEME 1. Energy Level Diagram of BPDH• in the Ground and Excited States and the Transient Processes



Similar spectral changes were observed for other BPDH• species. The relative intensities of the two peaks in the near-UV and visible regions changed with substitution on the phenyl ring (Figure 4). The peak in the visible region was broadened drastically in 4,4′-dimethoxy-, 4-methoxy-, 4,4′-difluoro-, and 4-fluorobenzophenone ketyl radicals in the D$_1$ states. It seems that the compounds with a large Stokes shift showed a relatively broad peak in the visible region. It is suggested that the electronic character of the substituent and the conformational change in the D$_1$ state affect the properties of BPDH•(D$_1$). It is also noteworthy that the absorption of methoxy-substituted BPDH•(D$_1$) in the near-UV region is blue-shifted and that of the visible region is red-shifted compared with the others. The structural change in the D$_1$ state is suggested to promote mixing between the higher excited doublet states.

All absorption decay curves were fitted well with the single-exponential decay function (Figure 2B). The τ values obtained from the transient absorption decay, summarized in Table 1, agreed well with those τ_f values.

Upon excitation with the second laser, the bleaching and recovery of BPH•(D$_0$) were observed (Figure 2C). The intermolecular reaction of BPH•(D$_1$) with the solvent molecules and the unimolecular cleavage of the O−H ketyl bond of BPH•-

(D_1), yielding benzophenone and a hydrogen atom, have been reported using nanosecond laser flash photolysis, while time evolution of the intermediate has not been observed because of the poor time resolution.[9,12] Thus, the decay of BPH•(D_1) observed in the present study can be attributed to the combination of a chemical reaction and nonradiative and radiative transition processes (Scheme 1). τ can be expressed as shown in eq 3

$$\tau = \frac{1}{k_C + k_f + k_{IC}} \tag{3}$$

where k_C is the rate constant of the chemical reaction and k_f and k_{IC} are the rate constants of the radiative and nonradiative relaxation processes from BPDH•(D_1), respectively. Because the chemical reaction does not regenerate BPDH•(D_0), the sum of k_f and k_{IC} is given by eq 4

$$1 - \frac{\Delta\Delta OD(t = \infty)}{\Delta\Delta OD(t = 0)} = (k_f + k_{IC})\tau \tag{4}$$

where $\Delta\Delta OD(t = 0)$ and $\Delta\Delta OD(t = \infty)$ refer to the $\Delta\Delta OD$ values immediately after and sufficiently after the second laser irradiation, respectively, estimated from the curve fitting. The k_C value can be estimated from eq 5

$$\frac{\Delta\Delta OD(t = \infty)}{\Delta\Delta OD(t = 0)} = k_C\tau \tag{5}$$

From these relations, the k_C and ($k_f + k_{IC}$) values for BPH•(D_1) were estimated to be 1.7×10^8 and 3.4×10^8 s^{-1}, respectively. The relative ratio for the chemical reaction (33%) and nonradiative and radiative processes (67%) of BPH•(D_1) was quite consistent with the reported value.[12] The k_C and ($k_f + k_{IC}$) values were also determined for BPDH•(D_1) species such as 4-bromo-, 4,4′-dichloro-, and 4,4′-dibromobenzophenone ketyl radicals (D_1). However, these values were not determined for other BPDH•(D_1) species because the recovery of BPDH•(D_0) was not observed due to the overlap of the $D_n \leftarrow D_1$ absorption, that is, BPDH•(D_1). No recovery of the transient absorption of BPDH•(D_0) was observed for the 4,4′-dimethoxybenzophenone ketyl radical (D_1) after the bleaching, although weak fluorescence was observed.

Substituent Effect on the Decay Processes of BPDH•(D_1). The τ values of the 4,4′-dichloro- and 4,4′-dibromobenzophenone ketyl radicals (D_1) were longer than those of BPH•(D_1) and the 4-bromobenzophenone ketyl radical (D_1). It is suggested that the longer τ values of those ketyl radicals (D_1) are attributed to the smaller ($k_f + k_{IC}$) values compared with those of BPH•(D_1) and the 4-bromobenzophenone ketyl radical (D_1). No recovery of the transient absorption of BPDH•(D_0) was observed for the 4,4′-dimethoxybenzophenone ketyl radical (D_1) after the bleaching, indicating that the chemical reaction is the main decay process. The relative ratios of the chemical reaction and the nonradiative and radiative processes of several BPDH•(D_1) species were significantly affected by the substituent on the phenyl ring.

Generally, τ increased with a decrease in the Stokes shift (Table 1). The $\Delta E(D_1 - D_0)$ values of BPDH• are similar, indicating that τ was not affected by the $\Delta E(D_1 - D_0)$ values. Therefore, it is suggested that BPDH•(D_1) species such as 4-fluoro-, 4,4′-difluoro-, 4-methoxy-, and 4,4′-dimethoxybenzophenone ketyl radicals (D_1), having shorter τ values and larger Stokes shifts, show higher reactivity with a larger k_C value. The distorted conformation in BPDH•(D_1) may enhance the reactivity.

Conclusions

The transient absorption spectra of a series of BPDH•(D_1) species were observed. The absorption spectrum of BPDH•(D_1) was significantly affected by the substituent on the phenyl ring. The lifetimes of BPDH•(D_1) were directly determined by fluorescence and absorption decays. The rate constants of the chemical reaction process competing with the nonradiative and radiative decay processes of BPDH•(D_1) were estimated from the depletion of the transient absorption of BPDH•(D_0). It is suggested that the factor which shortens the lifetimes of BPDH•(D_1) with a larger Stokes shift is the higher reactivity because of the distorted conformation.

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